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Removal of pharmaceuticals from WWTP effluent: removal of EfOM followed by advanced oxidation

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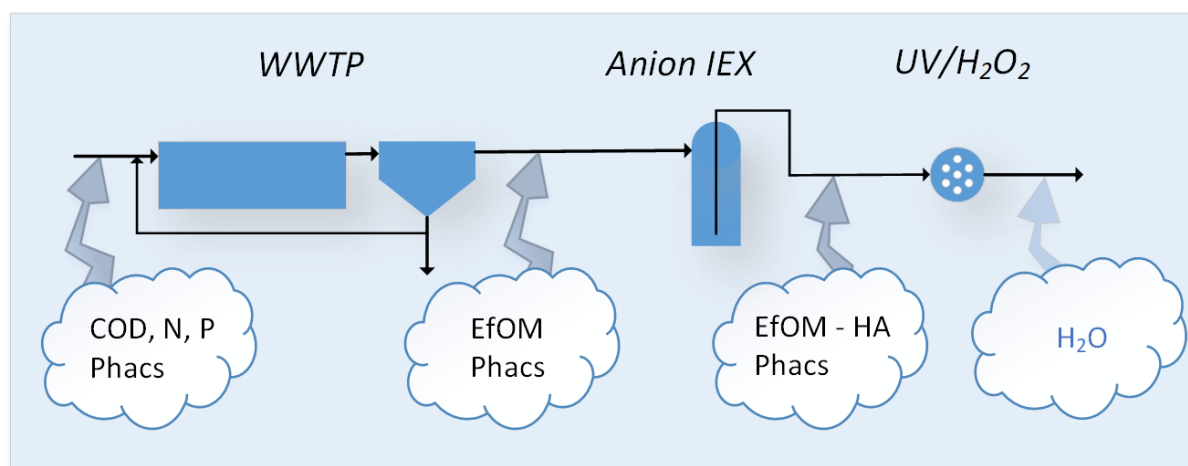
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Graphical Abstract



Highlights:

- WWTP effluent contains up to 20 mg/L dissolved non-biodegradable organic matter

- IEX can remove the humic acid fraction of effluent organic matter
- IEX+UV/H₂O₂ is robust process for pharmaceuticals removal from effluent
- After IEX, UV/H₂O₂ can be operated at a low dose of 300 mJ/cm²
- The energy demand of the UV/H₂O₂ process decreases by 84% after IEX

Keywords:

Pharmaceuticals, effluent organic matter, ion exchange, advanced oxidation, ozone/biofiltration, energy demand.

Abstract

Wastewater treatment plants (WWTPs) throughout the Netherlands contain significant concentrations of pharmaceuticals (25-65 µg/L) and about 10-20 mg C/L dissolved non-biodegradable organic matter. By means of IEX mainly the humic acid fraction of the effluent organic matter can be removed, whereas O₃/biofiltration mainly removes the hydrophobic fraction. For the first time the combination of these processes with O₃/H₂O₂, UV/H₂O₂ or UV/O₃ was tested for the removal of pharmaceuticals from wastewater effluent. Based on initial laboratory experiments, a pilot installation was built in which IEX followed by UV/H₂O₂ was applied to real WWTP effluent. The process appeared to be very robust, and able to remove a very broad range of different pharmaceuticals. The additional costs for this treatment are estimated at approximately €0.34/m³-treated effluent, which is in the same order of magnitude as estimated for other additional, but less versatile, treatment processes.

1. Introduction

Surface waters often contain a broad variety of organic micropollutants, like pesticides, industrial compounds, personal care products, steroid hormones, drugs of abuse and pharmaceuticals [1]. Increasing attention is being paid to pharmaceuticals, as these

compounds have been produced to affect living organisms at low concentrations. Many pharmaceuticals are very well soluble in water, partly because that makes it easier to administer them, partly also because the European REACH regulation stimulates the use of polar compounds [2]. Besides, little is known on the effect of long term exposure and of the presence of mixtures of pharmaceuticals. Their toxicity towards certain aquatic organisms, however, has clearly been demonstrated [3-5]. It is expected that the number and amounts of pharmaceuticals used will increase significantly in the coming years, due to demographic changes and climate change [6]. The major part of these compounds and their metabolites appear to leave the body via urine and feces, and thus will end up in municipal wastewater. However, wastewater treatment plants in general are designed to remove COD, nitrogen and phosphorous. On average WWTPs remove about 60-70% of the pharmaceuticals, but the removal of individual compounds can vary between 0 and 100%. The remaining pharmaceuticals end up in surface waters, where they can adversely affect the aquatic environment and may cause problems for drinking water production. In the river Meuse, it was found that the summed concentrations of a series of pharmaceuticals and their transformation products range from 4 to 38 µg/L [7]. From this study, it was concluded that 90% of the total pharmaceuticals load was determined by approximately 10 compounds and the other 10% comprised over 30 chemicals. Pharmaceuticals are not regulated at the moment in the EU, but in the 2013 amendment of the Environmental Quality Standards Directive (2008/105/EC) contains a mechanism to collect high-quality data on concentration of compounds of environmental concern, the so-called Watchlist. This list includes diclofenac, 17-Beta-estradiol (E2), and 17-Alpha-ethinylestradiol (EE2). For compounds on this list it is likely that regulations will be developed in future. This would mean that additional treatment of wastewater will be necessary to comply with these regulations. The Dutch Water Boards want to be prepared for this situation. Therefore, an increasing number of research projects is

being done into additional treatment steps for municipal wastewater. Examples are the use of activated carbon and of ozone [8-10]. Activated carbon is less effective for the adsorption of very hydrophilic, water soluble compounds [11], especially in case competition with more hydrophobic compounds like effluent organic matter occurs. In the Netherlands the use of ozone for drinking water treatment is limited because of the relatively high bromide concentrations in Dutch surface waters, as bromide is easily converted into the known carcinogenic bromate [12]. Besides, ozone preferably reacts with electron rich molecules, so not all pharmaceuticals thus can be degraded.

For drinking water production, advanced oxidation processes, e.g. based on UV/H₂O₂, have been proven to be very successful in dealing with a broad range of organic micropollutants [13-15]. However, WWTP effluent contains much more organic matter than drinking water. This organic material competes with the micropollutants in oxidation processes, as a result of which these processes will become less effective for removing micropollutants [1, 16]. Besides, in UV/H₂O₂ processes a high UV dose is required, typically around 500 mJ/cm², whereas for disinfection in general 20-70 mJ/cm² is sufficient. Because of the low UV transmittance of the effluent, the energy demand to reach such high doses will be very high. Therefore, it was studied whether the process can be optimized by removal of (part of) the Effluent Organic Material (EfOM) prior to the application of AOP. And although the EfOM removal processes and AOP are not novel techniques, it is for the first time that this combination is tested on treated wastewater effluent.

First, the EfOM was characterized and concentrations of a broad range of pharmaceuticals in Dutch WWTP effluents throughout the country were studied. Characterization of EfOM can be done in various ways. In principle EfOM consists of soluble non-biodegradable organic matter. A common method to characterize organic material is by means of LC-OCD techniques, which can (semi-)quantitatively determine the following fractions [17, 18]:

- Biopolymers (BP) with molecular weight (MW) $\gg 20.000$
- Humic substances (HS) with MW ≈ 1000
- “Building blocks” (BB) with MW $\approx 300-500$ (These are natural conversion products of humic substances)
- Neutral components with MW < 350 (LMW_n)
- Acidic components (LMW-acids) with MW < 350 (LMW_a)
- Hydrophobic organic compounds (HOC) (=DOC-BP-HS-BB-LMW_n-LMW_a)

According to Shon et al. EfOM contains 50% proteins, 40% carbohydrates, 10% fats and oils, and traces ($\leq \mu\text{g/L}$) of organic micropollutants [19]. In the present research, the LC-OCD method was applied. Additionally, the occurrence of a broad range of pharmaceuticals in the wastewater was determined.

Subsequently, in one particular wastewater two different techniques were applied to remove part of the EfOM: anion exchange (IEX), and ozone followed by biofiltration. It was decided to apply IEX as a pretreatment, and the effect of this pretreatment on a subsequent UV/H₂O₂ advanced oxidation process was studied both on laboratory and pilot scale. Although in principle advanced oxidation can result in total mineralization of the organic compounds, in most cases the degradation will occur to a lesser extent. In general, it is assumed that these (smaller) molecules will be better biodegradable [16]. However, it cannot be excluded that transformation products will be formed that might be even more toxic and/or persistent than their parent compounds [1], and thus should be taken into consideration too. To obtain information on this, the fate of some known metabolites during the treatment was studied too.

2. Materials and methods

2.1 Samples from WWTP effluents

Effluent samples were taken at various WWTPs throughout the Netherlands (Figure 1). The samples were collected with an automatic sample collector over 24 hours and proportional to the effluent flow rate, after several days of dry weather.

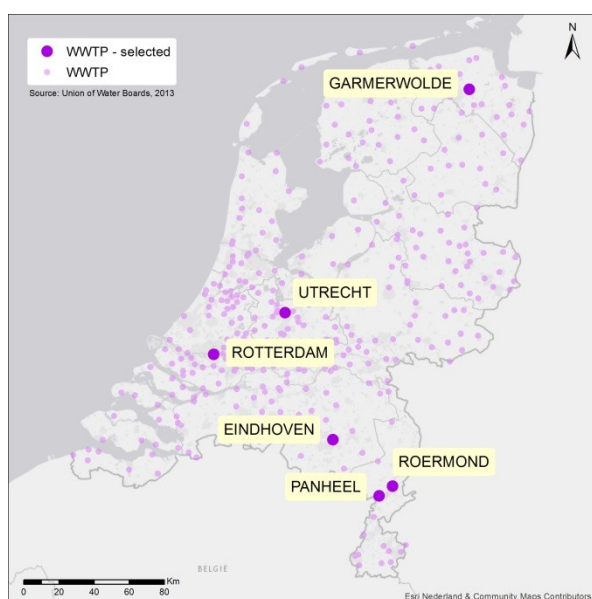


Figure 1: WWTPs studied.

TOC (Total Organic Carbon), DOC (Dissolved Organic Carbon) and UV-T (UV transmission at 254 nm) were measured at the KWR laboratory, and concentrations of a broad range of pharmaceuticals and some metabolites were measured according to the UPLC-MS/MS method described previously [13, 20]. The composition of the EfOM was determined by DOC-Labor Dr. Huber (Eisenbahnstr. 6, 76229 Karlsruhe, Germany), applying an LC-OCD method.

2.2 Laboratory experiments

Batch tests with the effluents of Panheel and Roermond had shown that the Lanxess S6368A resin (a strong base polystyrene) gave good results for EfOM removal. 300 L of water was filtrated over 10 L of resin at a flow of 10 bed volumes/min. For ozone/biofiltration different concentrations of ozone (0.15, 0.3 and 0.5 g O₃/g COD) were added to the effluent, followed by filtration over a biofilter (based on lignite coke carrying a biofilm) with a residence time of 15 or 30 min.

The laboratory experiments were conducted with effluent of WWTP Panheel, which was collected as a 24-hour flow proportional sample. Advanced oxidation experiments were carried out after pretreatment with 15.3 mg O₃/L (i.e. 0.3 g O₃/g COD) and a hydraulic retention time (HRT) in the biofilter of 15 min. IEX was applied using a column filled with Lewatit S6368A, provided by Lanxess AG (Kennedyplatz 1, 50569 Cologne, Germany). A mixture of over 30 pharmaceuticals was added according to the method described in [13, 20], at concentrations of 1 – 5 µg/L (100 * the reporting limit of the analysis), as concentrations in WWTP effluent may show variations, and the concentrations had to be high enough to be able to determine their degradation. Metabolites were analyzed, but had not been dosed to the water. 10 mg/L H₂O₂ (JT Baker; Baker analyzed; CAS nr. 7722-84-1) was added to the solution. 100 ml solutions were treated with a low-pressure mercury UV lamp (Philips PLL60W) in a collimated beam apparatus. The distance between the lamp and the irradiated surface was 30 cm, doses applied were 0, 300, and 600 mJ/cm². In another experiment first H₂O₂ and then ozone was added to a mixture of the pharmaceuticals, resulting in a concentration of 36 mg H₂O₂/L and an ozone dose of 12.5, 31.2 or 62.4 mg/L. The third experiment combined the same ozone doses with a UV dose of 120-150 mJ/cm² in a flow-through reactor equipped with a 90 W UV lamp.

2.3 Pilot experiments

The pilot plant consisted of multi-layer filter column for particles and suspended solids removal from the WWTP effluent. The filter rate operated at a rate of 25 m/h. The filtration set-up was backwashed with filtered water (influent over a 150 μm filter) after reaching a maximum head loss setpoint. The filtered water was stored in a 1,000 L vessel, continuously flowing over near the WWTP effluent sampling point.

The anion IEX unit consisted of two IEX vessels, each containing 25 L of Lanxess type Lewatit S6368A. The contact time of the water in the IEX was 2 minutes (flow 750 L/h). For the pilot experiments also a wide range of pharmaceuticals was added to the water, in concentrations of 1 – 5 $\mu\text{g/L}$ (100 * the reporting limit of the analysis), also to be sure concentrations are high enough to determine significant degradation. Metabolites were analyzed, but had not been dosed to the water. The IEX treated water is, in case of dosage of the pharmaceuticals, fed to the UV/H₂O₂ set-up. The overflow of the IEX was discharged. After passage of 7,000 L of pretreated effluent water, the IEX was regenerated with an aqueous solution of about 10 wt-% NaCl (Broxo). After flushing the bed to remove the salty water, the IEX is ready to be used again.

The UV/H₂O₂ set-up was operated discontinuously and only during the spiking of pharmaceuticals. Influent of the UV/H₂O₂ system was collected into the influent vessel of 200 liters. Hydrogen peroxide was dosed manually into the vessel. The UV system was equipped with a low-pressure Amalgam lamp of 90 W in a M3 UV reactor system of PureBlue Water. During different tests, UV₂₅₄ absorbance was measured and the dose of 150 or 300 mJ/cm^2 was set with a flow controlling system (flow $\leq 1 \text{ m}^3/\text{h}$). The UV reactor also had been equipped with a 30 W Ultrasound (US) device. However, it was shown that this didn't

contribute to the conversion of pharmaceuticals (see supplementary information). A largely over-dimensioned granular activated carbon (GAC) filtration unit consisting of 2 columns filled with Norit activated carbon (type PK 1-3) was used to treat the pilot effluent water before discharging it to the surface water. The activated carbon filtration (ACF) is not used in this research to study the effects of ACF for the removal of pharmaceuticals.

3. Results and Discussion

3.1 Analyses of WWTP effluents

The EfOM composition in various WWTP effluents is shown in Figure 2 (top). Clearly, the effluents from Garmerwolde, Panheel and Roermond contain significantly more EfOM than the other three effluents. This shows that “large” variations are possible. From Figure 2 (bottom) it also can be concluded that all effluents contain significant amounts of pharmaceuticals. A detailed overview of all pharmaceuticals analyzed can be found in the supplementary information. The main compounds are Metformin and its transformation product Guanylurea (which is formed by the WWTP sludge), which appear in concentrations of $> 10 \mu\text{g/L}$ (up to about $30 \mu\text{g/L}$ in Panheel). This clearly shows that the presence of pharmaceuticals in effluent, and thus in surface water, cannot be neglected.

In the samples analyzed for this research pharmaceutical concentrations varied from about 25 to $70 \mu\text{g/L}$. By spiking the pharmaceuticals a total load $< 40 \mu\text{g/L}$ was added, which means that the total concentration of pharmaceuticals still were in the same order of magnitude. As EfOM concentrations are a factor 1000 larger than the concentrations of pharmaceuticals, it is to be expected that this addition won't have affected the processes themselves.

3.2 Effect of pretreatment on EfOM composition

Two types of pretreatment were studied: IEX and O₃/biofiltration. Ozone can react with electron rich compounds, making them better biodegradable. This is shown in Table 1: the chemical oxygen demand (COD) of the water decreases upon ozone treatment, and even more after subsequent biofiltration. Furthermore, it can be observed that there is no significant change of the TOC content due to ozonation. Compounds may be degraded at the ozone dose used, but the reaction products will not disappear, contrarily to the effect of biodegradation. This also is reflected in the increase in UV-T upon ozonation and subsequent biofiltration. IEX results in a significant increase in UV-T too. The effect of a UV-T improvement on the energy demand of a UV/H₂O₂-process can be large, as can be concluded from Table 3 (calculations based on the model of Bolton [21-23]).

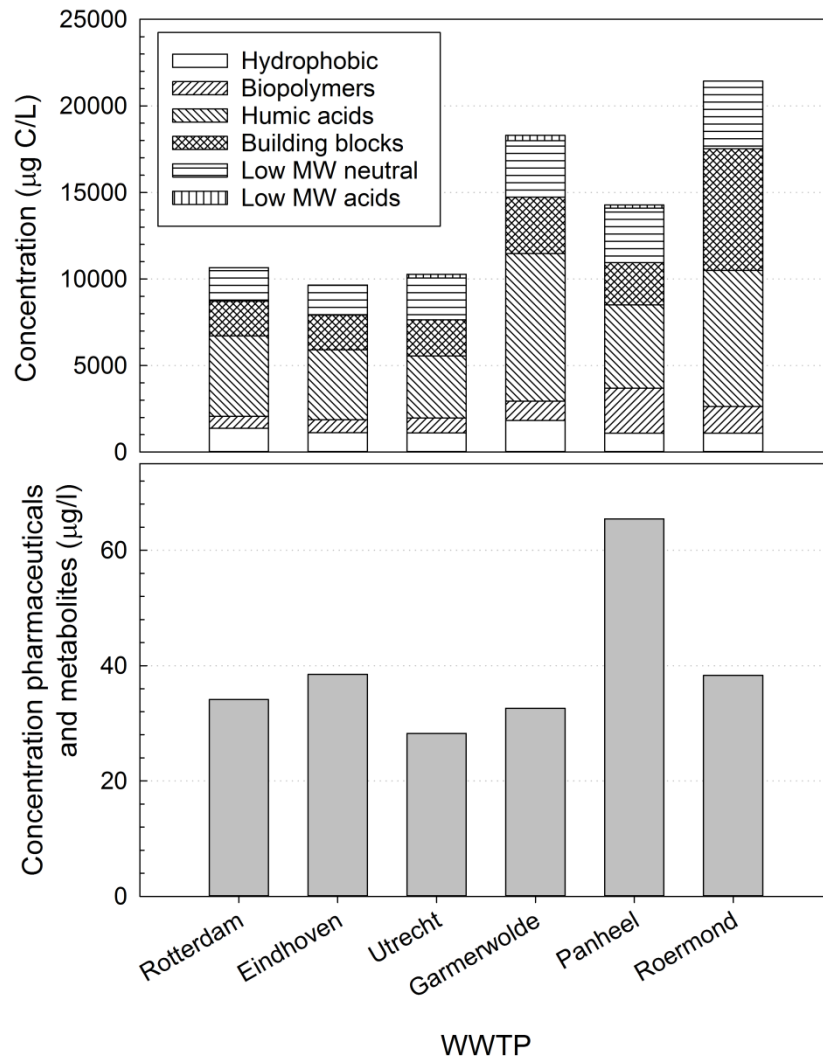


Figure 2: Composition of effluents. Upper panel: composition of EfOM. Lower Panel: total concentration of pharmaceuticals present (Summer 2014). More details on the type and concentrations of pharmaceuticals can be found in the supplementary information.

Table 1: Effect of ozonation and subsequent biofiltration on the characteristics of the effluent of Roermond. HRT = hydraulic retention time in biofilter.

Ozone	after O ₃			HRT=15 min.			HRT=30 min.	
concentration								
(mg/L)								
	COD	TOC	UV-T	COD	TOC	UV-T	COD	UV-T
	(mg/L)	(mg	(%)	(mg/L)	(mg	(%)	(mg/L)	(%)
		C/L			C/L			
0	62	20	22.7	40	10	40.8	35	47.5
9.3	57	21	28.9	35	9.2	40.4	32	47.8
18.6	51	21	34.2	33	11	48.4	29	51.2
24.5	49	21	38.1	32	9.7	52	28	56.6

Table 2: Effect of improvement in UV-T in Panheel effluent on relative energy demand of a UV-process.

Type of water	UV-T (%)	Relative energy demand of UV process
Effluent Panheel	38	100%
After O ₃ /biofiltratie	69	38%
After IEX	85	16%

From Table 2 it can be concluded that it may be worthwhile to remove (part of) the EfOM in order to make a UV-process more energy efficient.

The effect of ozone/biofiltration and IEX pretreatment on the EfOM composition in the Roermond and Panheel effluents is shown in Table 3.

Table 3: Effect of pretreatment on the composition of effluent of Roermond and Panheel.

Sample	Process	Process step	HOC (µg/L)	BP (µg/L)	HS (µg/L)	BB (µg/L)	LMWn (µg/L)	LMWa (µg/L)	Total (µg/L)
Roermond (06/2014)	--	Effluent	1093	1544	7865	7031	3897	0	21430
		Effluent	2315	1236	12592	8315	4429	1	28888
		After O ₃ (15.3 mg/L)	1194	1002	7486	4087	2824	1	16594
Roermond (09/2014)	O ₃ /biof.	After biof. (HRT 15	1155	817	4980	2523	1298	1	10774

		min.)							
		<i>Total</i>	<i>50</i>	<i>34</i>	<i>60</i>	<i>70</i>	<i>70</i>	<i>0</i>	<i>63</i>
		<i>removal</i>							
		(%)							
Panheel	--	Effluent	1090	2595	4821	2443	3143	190	14282
(06/2014)									
		Effluent	795	1162	4040	1251	1676	245	9169
		After	0	606	2404	1033	895	53	4991
Panheel		O ₃ /biof.							
Lab.	O ₃ /biofil.	(10 mg/L;							
(09/2014)		HRT 6							
		min.)							
		<i>Total</i>	<i>100</i>	<i>48</i>	<i>40</i>	<i>17</i>	<i>47</i>	<i>78</i>	<i>46</i>
		<i>removal</i>							

		(%)						
		effluent	795	1162	4040	1251	1676	245 9169
		After IEX	365	891	0	471	916	304 2947
IEX		<i>Total</i>	54	23	100	62	45	-- 68
		<i>removal</i>						
		(%)						
		effluent	2108	1953	5167	1995	2847	0 14070
		After	1935	1921	5105	2042	2859	0 13862
Panheel		filtration						
Pilot	IEX	After IEX	909	1960	0	1898	2379	792 7938
(01/2016)		<i>Total</i>	57	--	100	5	16	-- 45
		<i>removal</i>						
		(%)						

Table 3 shows that there can be large differences in effluent composition and content between WWTPs. Also between samples taken at different times large differences in composition at the same WWTP can be observed. Furthermore, in the Roermond sample ozone oxidizes about half of the HOC, HS and BB present, and about 19% of BP and 36% of LMWn. Additional biofiltration mainly removes LMWn (ca. 54%), and about 35% of HS and BB. In total about 45-65% of the EfOM can be removed applying O₃/biofiltration. At the Panheel site 100% of HOC was removed in Autumn 2014, and about 50% of BP, HS and LMWn. IEX removes 100% of HS, >50% of HOC, even though HOC was not expected to be charged. Like O₃/biofiltration, IEX can also remove about 45-65% of the EfOM in total, although the composition of the resulting material differs in both cases. The multi-layer filtration hardly contributed to the removal of EfOM. For practical reasons, it was decided to continue experiments at the pilot plant with IEX as pretreatment.

Pretreatment (by means of O₃/biofiltration or IEX) may also affect the pharmaceuticals present in the effluent. To check this, a mixture of pharmaceuticals was added before pretreatment. The resulting removal is shown in Figure 3.

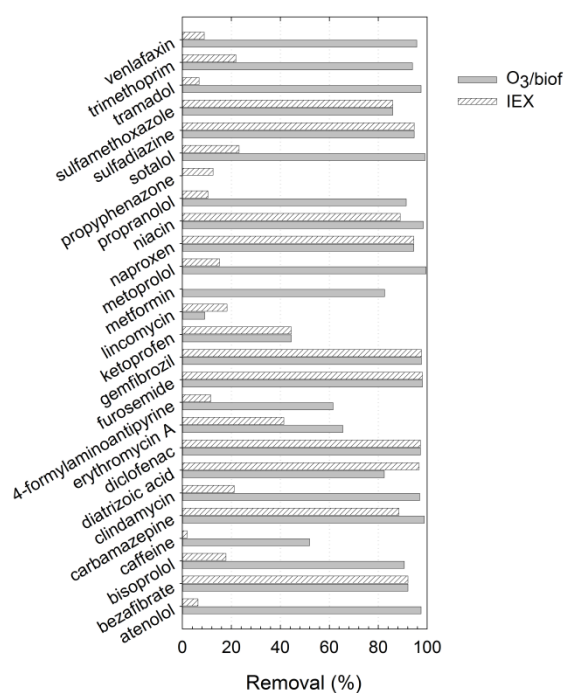


Figure 3: Removal of pharmaceuticals by pretreatment

Obviously, compounds carrying a negative charge at this pH (ca. 7.5) can be effectively removed by IEX. As expected, also ozone/biofiltration can be very effective, depending on the compounds molecular structure.

3.3 Effect of pretreatment on subsequent advanced oxidation processes

The degradation of pharmaceuticals in WWTP effluent (without pretreatment) by three types of advanced oxidation processes (O₃/H₂O₂, UV/H₂O₂ and UV/O₃) is shown in Figure 4. For some compounds (salbutamol, propyphenazone, niacin, lincomycin, erythromycin A, caffeine, and sulfachloropyridzine) it seemed to be difficult to obtain reliable analyses, especially for the O₃/H₂O₂ and the UV/H₂O₂ process. The problem didn't seem to occur with the UV/O₃ process. Possibly, the presence of other compounds in the effluent interfered with the analyses.

In untreated effluent, with a very low UV-T, the O₃/H₂O₂ process may be quite efficient.

Under the conditions applied, most compounds show a conversion >80%. At the lowest O₃ dose only for diatrizoic acid, metformin and sulfachloropyridazine lower conversions were obtained, but they increased with increasing ozone dose. Partly the high conversions can be attributed to the relatively high H₂O₂ concentration of 36 mg/L, as from Figure 4 (right) it can be seen that even a concentration of 10 mg/L may already degrade diclofenac, furosemide, naproxen and phenazone to over 90% under these conditions. For the other compounds in the UV/H₂O₂ process obviously degradation increases with increasing UV dose, although not all compounds reach a degradation level ≥80%, as would be required.

Remarkably, the UV/O₃ process seems to give the highest degradation levels, even though the UV-T of the water is very low. Only for metformin degradation would be too low.

To study the effect of the presence of EfOM on the removal of pharmaceuticals, IEX pretreatment was applied prior to both the O₃/H₂O₂ and the UV/H₂O₂ process. The results of these experiments are shown in Figure 5. For the O₃/H₂O₂ process the effect of removal of part of the EfOM is relatively small: only for some compounds, like cyclophosphamide and diatrizoic acid the process becomes significantly more efficient. However, it can be seen that the removal of a part of the EfOM largely affects the UV/H₂O₂ process. Furthermore, after IEX pretreatment a UV dose of 300 mJ/cm² seems to be high enough to obtain sufficient removal of most pharmaceuticals tested. The amount of energy required to obtain this dose also has decreased significantly, according to Table 2.

Based on these results it was decided to build a pilot set-up at the WWTP of Panheel, applying IEX as pretreatment and UV/H₂O₂ as AOP. The UV dose was set to either 150 or 300 mJ/cm². The results are shown in Figure 6.

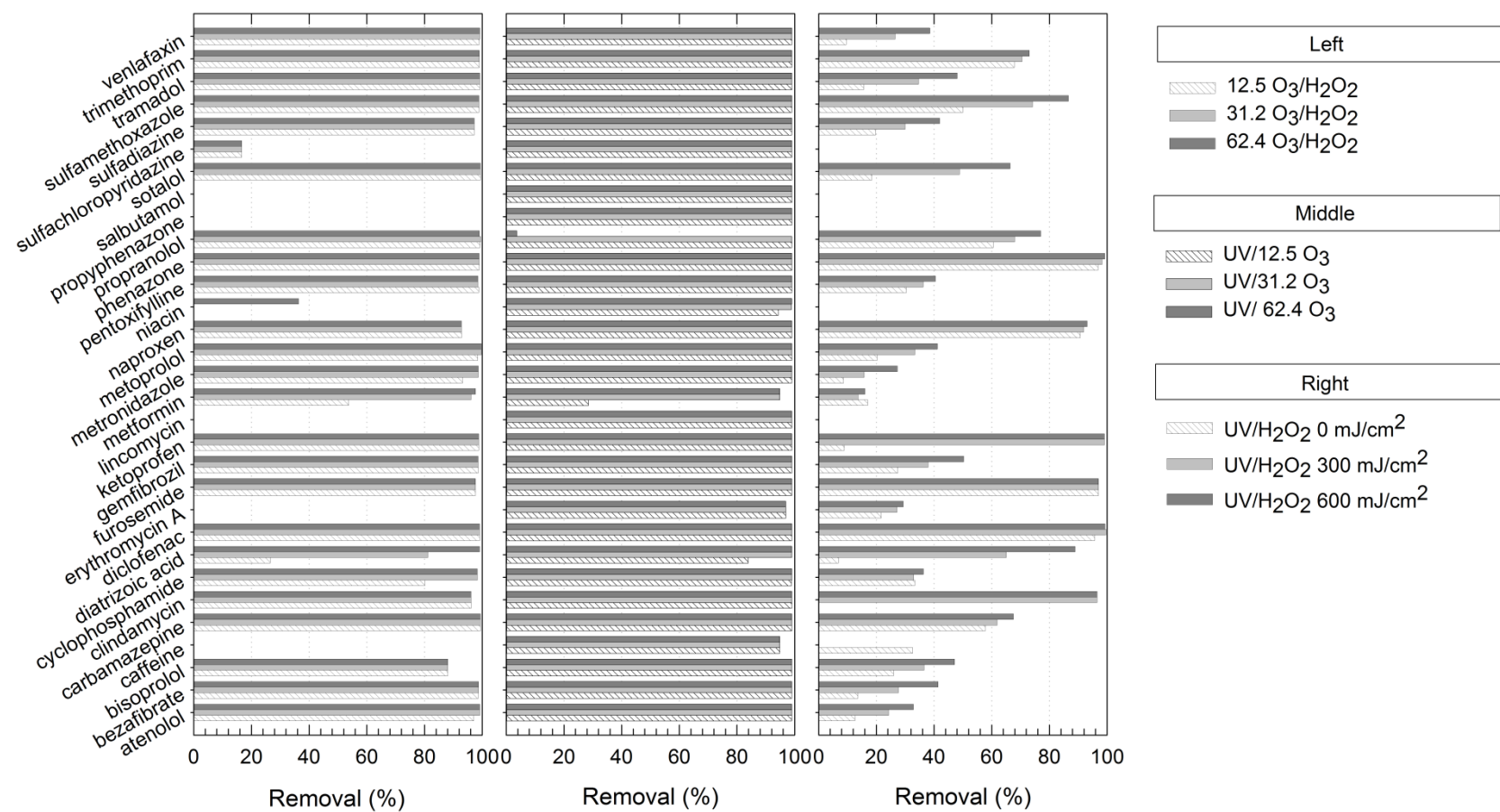


Figure 4: Conversion of pharmaceuticals in untreated effluent by AOPs. Left: O_3/H_2O_2 (36 mg H_2O_2/L); Middle: UV/ O_3 ; Right: UV/ H_2O_2

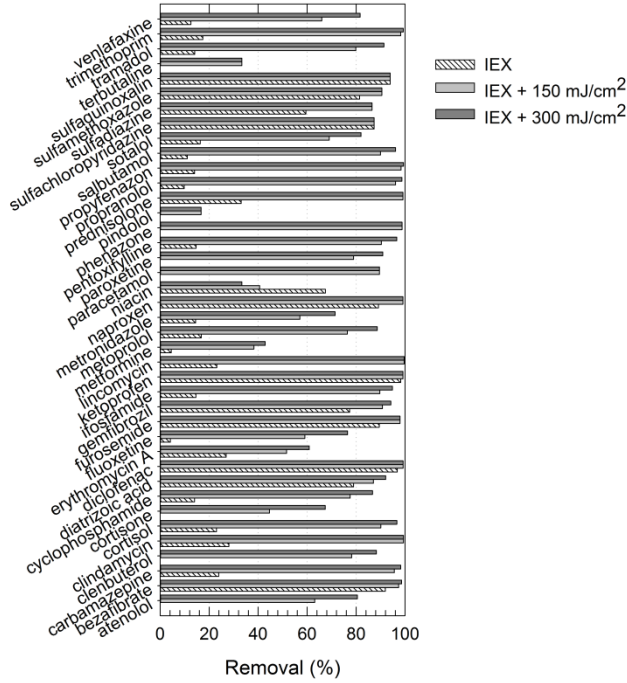


Figure 6: Total removal of pharmaceuticals by means of IEX, or IEX followed by UV/H₂O₂ (150 and 300 mJ/cm²) in pilot experiments

Again, it was found that the concentrations of most pharmaceuticals tested could be significantly decreased. For most compounds tested a UV dose of 150 mJ/cm² would already be sufficient to obtain enough removal of pharmaceuticals. This is an extremely low UV dose for an AOP process, as even in drinking water production UV doses of about 500 mJ/cm² are common in UV/H₂O₂ processes [20]. The effect of pretreatment can clearly be seen in the Electrical Energy per Order (E_{EO}):

$$E_{EO} = \frac{P}{F \cdot \log\left(\frac{C_i}{C_e}\right)} \quad \text{eq. 1}$$

In this formula P is the electrical power (W), F is the flow through the reactor ($\text{m}^3 \text{s}^{-1}$), C_i is the concentration in the influent (mg L^{-1}) and C_e is the concentration in the effluent (mg L^{-1}).

The effect on E_{EO} -values is shown in Figure 7:

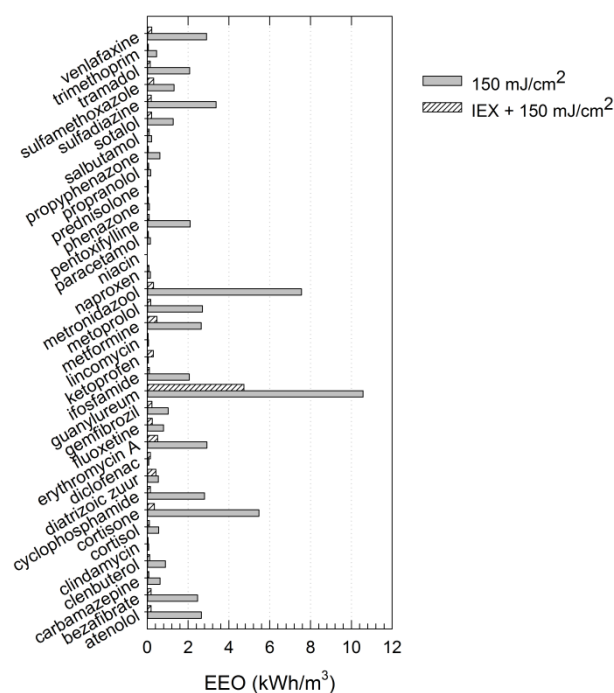
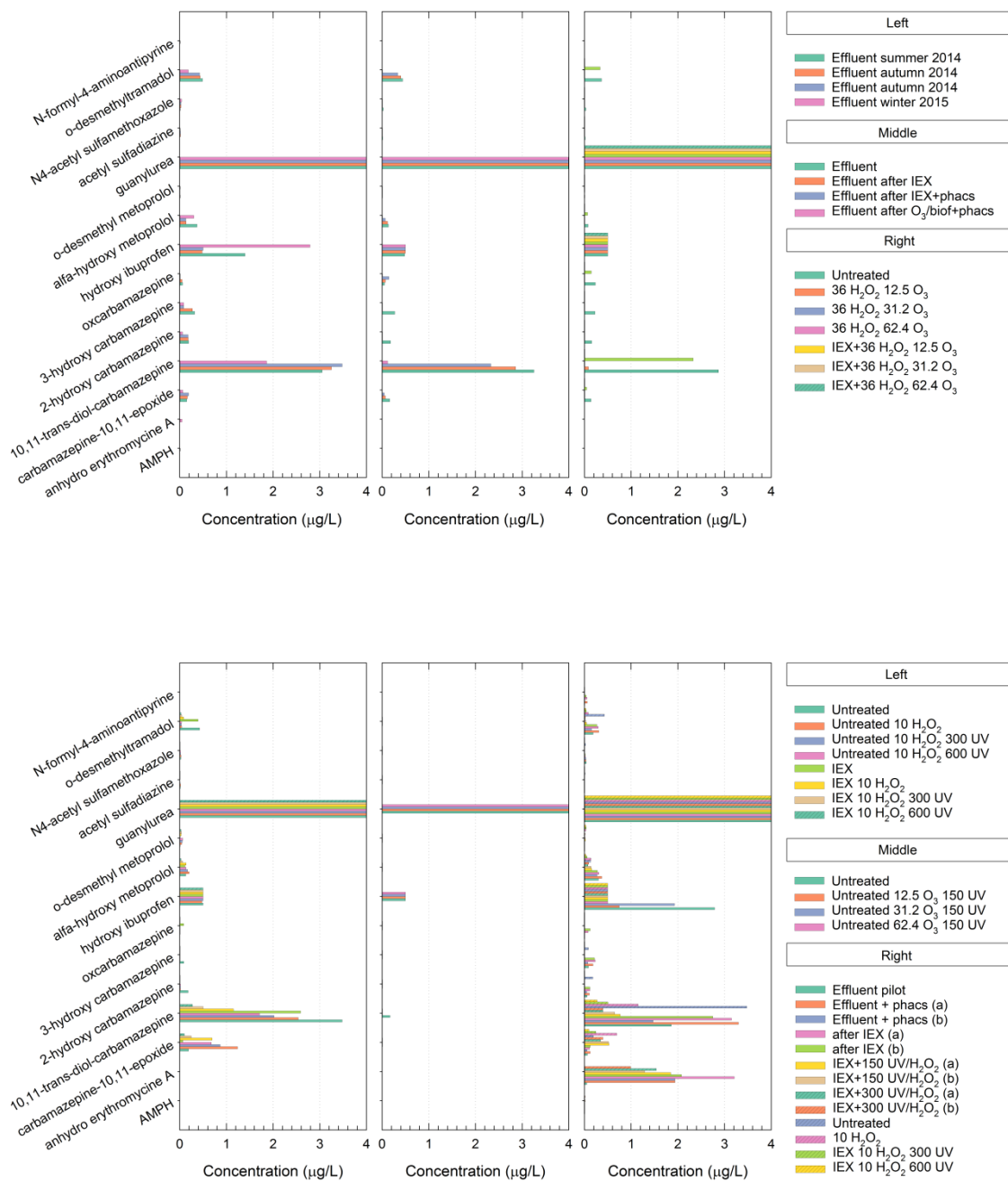


Figure 7: E_{EO} values of UV/ H_2O_2 process without pretreatment and after IEX (only compounds which had been removed $<80\%$ by IEX were considered)

In Figure 7 only those compounds for which IEX showed a removal $<80\%$ were considered. This was done because otherwise E_{EO} values are difficult to determine because concentrations reach the reporting limit. Obviously, the IEX pretreatment has a huge effect on the E_{EO} values, and thus on the amount of energy required for the UV/ H_2O_2 process. This shows that the presence of humic acids has a large effect on the efficiency of the UV/ H_2O_2 process.

3.4 Fate of metabolites

Special attention was paid to metabolites present in the effluent before and after treatment (supplementary information Tables supp-1 till supp-5 refer to the laboratory experiments, Table supp-6 to the pilot tests). A summary of the results is shown in Figure 8. As can be concluded from Table supp-1, the concentration of metabolites may vary largely with time. Treatment of the effluent with IEX may remove part of the metabolites, but it is not effective for O-desmethyltramadol, guanylsurea, hydroxyl-ibuprofen and 10,11-trans-diol-carbamazepine. O₃/biolfiltration is more effective in the removal of metabolites, except for guanylsurea and hydroxyl-ibuprofen (Table supp-2). The same conclusion can be drawn for the O₃/H₂O₂ process, with or without IEX (Table supp-3), and the UV/O₃ process (Table supp-4). Addition of only H₂O₂, with or without IEX pretreatment, resulted in an increase in the amount of carbamazepine-10,11-epoxide, but for all other metabolites analyzed the concentrations decreased. Probably, oxidation by H₂O₂ resulted in the formation of this metabolite. However, applying UV irradiation in combination with H₂O₂ resulted in a lower concentration of metabolites, the concentrations decreasing with increasing UV dose (Table supp-5). Similar results were obtained in the pilot set-up (Table supp-6 and Figure 8). Thus, it can be concluded that advanced oxidation, with or without pretreatment, did not result in the formation of known metabolites.



4. General discussion

For the first time IEX followed by UV/H₂O₂ was tested as an additional treatment step for removing pharmaceutical compounds from biologically treated waste water effluent. The energy demand of the UV/H₂O₂ process decreases by 84% after application of IEX, making the process extremely attractive for application in practice.

For the WWTP Panheel, an outline design for a full-scale application was made with a total capacity of 1,825 Mm³/year. Costs were calculated applying the Community of Practice Cost Calculator of RHDHV (www.kostenstandaard.nl) taking into account an additional pumping stage to create sufficient hydraulic head and ACF. The total extra costs would be about €0.34/m³ of treated effluent, including depreciation and operating costs. Recently, Mulder, Antakyali and Ante [24] compared processes studied in Germany and Switzerland, based on ozone, PAC or GAC, followed by rapid sand filtration (RSF), and calculated additional costs of about €0.30-0.40/m³, which are in the same order of magnitude. However, UV/H₂O₂ can be applied to remove a broad range of organic micropollutants, whereas ozonation converts mainly electron rich components, and ACF preferably adsorbs non-polar, hydrophobic compounds. Therefore, we expect that IEX followed by UV/H₂O₂ is more versatile. It is expected that the removal of the humic acid fraction, which accounts for about 50% of the total EfOM, will negatively affect surface water composition, on one hand because of the large variations in river discharge, which account for more than this difference, and on the other hand as humic acids are rather inert materials, which e.g. in soil are used to improve the textural quality of the soil [25].

5. Conclusions

It was shown that WWTP effluent contains significant concentrations of pharmaceuticals (25-65 µg/L) and about 10-20 mg C/L organic matter. By means of IEX mainly the humic acid fraction of the effluent organic matter can be removed, whereas O₃/biofiltration mainly removes the hydrophobic fraction. IEX pretreatment results in an increase in UV-T from 38 to 85%, resulting in a decrease in energy demand for the UV/H₂O₂ process of 84%. During pilot tests the IEX-UV/H₂O₂ process proved to be a robust process, able to remove a very broad range of different pharmaceuticals to a high extend. The additional costs for this treatment are estimated to be about €0.34/m³, which is in the same order of magnitude as was estimated for other additional treatment processes, like ozonation or ACF, followed by RSF.

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7. References

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